COVER SHEET

Effects of substrate curvature on the adsorption of Poly(3-hexylthiophene) on Single Walled Carbon Nanotubes

Roland G.S. Goh, Nunzio Motta*,John M. Bell

Centre for Built Environment and Engineering Research, Queensland University of Technology, GPO Box 2434, Brisbane, AUSTRALIA, 4001

Eric R. Waclawik

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane, AUSTRALIA, 4001

(Revised version - 14 november 2005)

A detailed study of poly(alkylthiophene) self-assembly and organization on single-walled carbon nanotubes (SWNTs) is presented. Monolayers of regioregular poly(3-hexyl thiophene) (rrP3HT) adsorbed on SWNTs have been imaged by scanning tunneling microscopy. Our results show that the rrP3HT interchain distance is greater for rrP3HT monolayers adsorbed onto the curved surfaces of SWNTs than on the flat surfaces of highly ordered pyrolytic graphite samples. Comparisons between the native polymer deposited on graphite and the composite structure confirmed that the presence of carbon nanotubes in rrP3HT produces a material with a high degree of order at the molecular level.

- Corresponding author: n.motta@qut.edu.au

Conjugated polymer composites are promising candidates for use as the active material in organic electronic devices. However a composite's nanoscale architecture can profoundly affect device performance. Hence control of the organic component's molecular order is critically important[1].

The strong dependence of the optical and electrical properties of conjugated systems on nanoscale structural organization is now well recognized[2]. It was recently demonstrated that carbon nanotubes inclusion can sometimes increase the effective crystallinity of conjugated polymers[3,4,5], and that their inclusion in poly(*m*-phenylenevinylene) (PmPV), creates a composite material possessing both enhanced electrical conductivity[6] and mechanical strength[7]. Poly-(alkylthiophene)/carbon nanotubes mixtures have been recently studied as they are promising materials for use in organic photovoltaic and optoelectronic memory devices[8,9]. Poly(3-hexylthiophene) (P3HT) is a particularly interesting model system in which to study epitaxial and bulk structures that arise during composite formation because when head-to-tail coupled (regioregular form) the native polymer possesses a remarkable charge transport mobility (0.1 cm^2/Vs)[10] that is dependent upon non-covalent, intermolecular interactions within the polymer itself.

The way in which polymers are attached to carbon nanotubes has been investigated by various authors, leading to two contradictory conclusions: Lei et al.[11] suggests that the arrangement is dominated by the matching of the graphene hexagonal structure with the detailed structure of the conjugated polymer, while Coleman and co-workers[12] have pointed out that geometric factors and constraints imposed by a narrow cylindrical structure, like a SWNT on a conjugated polymer chain, may outweigh any lattice-resolved contributions to polymer ordering. To better understand this issue, we have studied by STM the organization of the conjugated polymer rrP3HT on SWNT and on highly oriented pyrolitic graphite (HOPG).

Since a SWNT can be considered as a seamless rolled-up sheet of graphene, a comparison between STM measurements of P3HT/SWNT composites and P3HT-coatings on HOPG should be used to

separate atomic surface structure from geometric factors (graphene curvature) in P3HT ordering. Hence, we performed STM investigations of rrP3HT films cast from chloroform solutions onto HOPG. We investigated drop-cast films of rrP3HT solutions with low (~1μg/ml) and high (~4mg/ml) polymer concentration, the latter being a concentration equivalent to those used for the rrP3HT/SWNT composites. To date, STM studies of conducting polymers which have revealed details of polymer-monolayer chain folding and self assembly have usually been performed with dilute solutions deposited on HOPG[11,13,14]. However, polymer composite films used in organic electronic devices are typically cast from more concentrated solutions (on the order of 1 mg/ml or greater), and bulk effects are likely to be affecting their organization and assembly[15].

Fig 1a shows a rrP3HT monolayer film cast from a diluted solution of chloroform where the polymer chains are clearly aligned in rows on the HOPG surface. The measured chain to chain distance is 1.45 nm, within the range of those measured by Mena-Osterlitz et al.[13]. The presence of 60º and 120º folds is evidenced by the dark grey lines (blue online) on the image.

The STM images of P3HT thick coating (Fig 1b-1c) on graphite appear as a fairly uniform film at the microscale. Most of the surface is covered by a thick layer, but in some small areas we were able to resolve the underlying flat lying polymer layer. Linear strands and folded chains could clearly be observed (boxed region of Figure 1b) in these areas, suggesting 2D ordered assembly in the adlayer just below the thick aggregates.

However, because of the thick coating, most of the surface is covered by bright islands approximately 2nm higher than the folded chains (Figure 1b). This could correspond to approximately one lamella sitting on top of the background layer with π-stacking normal to the substrate and the plane of the thiophene rings normal to the substrate, as found when the polymer is deposited by repetitive dip-coating[15,16] via a Langumuir-Blodgett technique. The total layer thickness is about 4 nm as apparent from Fig 1c. The STM results displayed in Figure 1 are thus a confirmation of the proposed Stranski-Krastanov type mechanism for the formation of these films.

Figure 2 shows P3HT/SWNT composites imaged at various length-scales using STM. The high aspect ratio of SWNTs allows them to be easily located by STM, even when covered with rrP3HT polymer. It is immediately apparent from Figures 2a that there is an abundance of rod-like features throughout the composite which we interpret as being SWNTs obscured by thick polymer coatings. In Figure 2b a fairly long tube with ends pinned by polymer islands is visible, along with a short tube of about 30nm lying adjacent to it. A magnified view of this tube is shown in Figure 2c, where it can be seen that the polymer coats the tube evenly over its length. The diameters of the carbon nanotubes used in this study are ~1.4nm as determined from Raman spectroscopy[17]. With the π-π stacking distance of the polymer being estimated to be 0.38nm[16], and taking into consideration the van der Waals radius, a monolayer-wrapped tube should be 2.16 nm thick[18]. Measured tube heights vary between 2.1 and 2.5 nm, matching the expected value for the diameter if we include the nanotube-substrate distance of 0.25 nm; hence we believe these objects to be individual single-walled carbon nanotubes coated with one layer of polymer. The rod-shaped features are thus likely to be rrP3HT-coated SWNTs with lengths ranging from tens of nanometers to about 200 nanometers.

A high a degree of rrP3HT polymer chain organization, *i.e.* polymer wrapping, can be seen along the entire tube axis. This confirms the view that when ultrasonically-dispersed in a polymer solution, the nanotubes absorb as many strands of polymer as possible to reduce interactions with adjacent tubes[18]. The cross section measurement along the axis (left graph) reveals a periodicity of approximately 1.66nm, substantially larger than the polymer chain-to-chain distance of 1.45nm found in Fig.1a on HOPG: notice that this latter value agrees with the one of ~1.4nm measured on HOPG by Grévin et al[14]. Measurements of several tubes yielded an average chain-to-chain distance of 1.68 ± 0.02 nm. The larger value measured on nanotubes with respect to that found on HOPG may indicate that the substrate curvature is playing a fundamental role in assembly of ordered domains[12]. The role of curvature on monolayer formation was also recently demonstrated in

dramatic STM images of monolayer protected nanoparticle surfaces[19], underlining the importance of factors such as geometrical constraints and surface stress anisotropy.

In addition, measurements of the chiral angle of polymer wrapping with respect to the nanotube long-axis were extracted from the STM scans (Fig. 3a), where individual rrP3HT thiophene chains are resolved. The value measured here is 48º(±4º), while in Fig 2c we have obtained 41º(±4º). Polymers have usually been observed to wrap the tubes with a chiral angle with respect to the tube axis, suggesting a connection to the underlying chirality of the tube[20]. For PmPV a purely geometrical explanation without regard to the chirality was proposed by Coleman *et al* [12] . This model works because PmPV is a "stiffer" polymer compared to P3HT (10nm persistence length[12] compared to 2.1nm for P3HT[21]). The periodic potential of the hexagonal lattice[22] is instead expected to play an important role in the geometrical arrangement of P3HT. The different measured interchain distances and chiral angles observed for individual rrP3HT-coated nanotubes suggest that at least for the case of rrP3HT composites, carbon nanotube chirality could significantly influence the polymer structures depositing at the surface. This however does not rule out other possibilities like that of polymer alignment lengthways along the tube. Electronic effects may very well be predominant in the interactions of polymers with the small diameter single-wall carbon nanotubes.

In summary, we have imaged by STM the arrangement of rrP3HT on HOPG and nanotubes. While 2D crystals are observed when rrP3HT is cast onto HOPG from dilute solution, we have found a thicker and more disordered film when cast from our concentrated solutions. The subsequent layers are more likely to align normal to underlying monolayer on HOPG. In nanotube/polymer mixtures rrP3HT chains have the tendency to wrap around SWNTs, where thiophene and hexyl moieties associate with the nanotube surface in identical manner to rrP3HT monolayer depositions on HOPG. We have performed measurements of the chain to chain distance, finding an average value on SWNTs (1.68 nm) 20% larger than on HOPG. It is likely that the measured differences of interchain-spacing arise because of the substrate curvature. Further studies are in progress.

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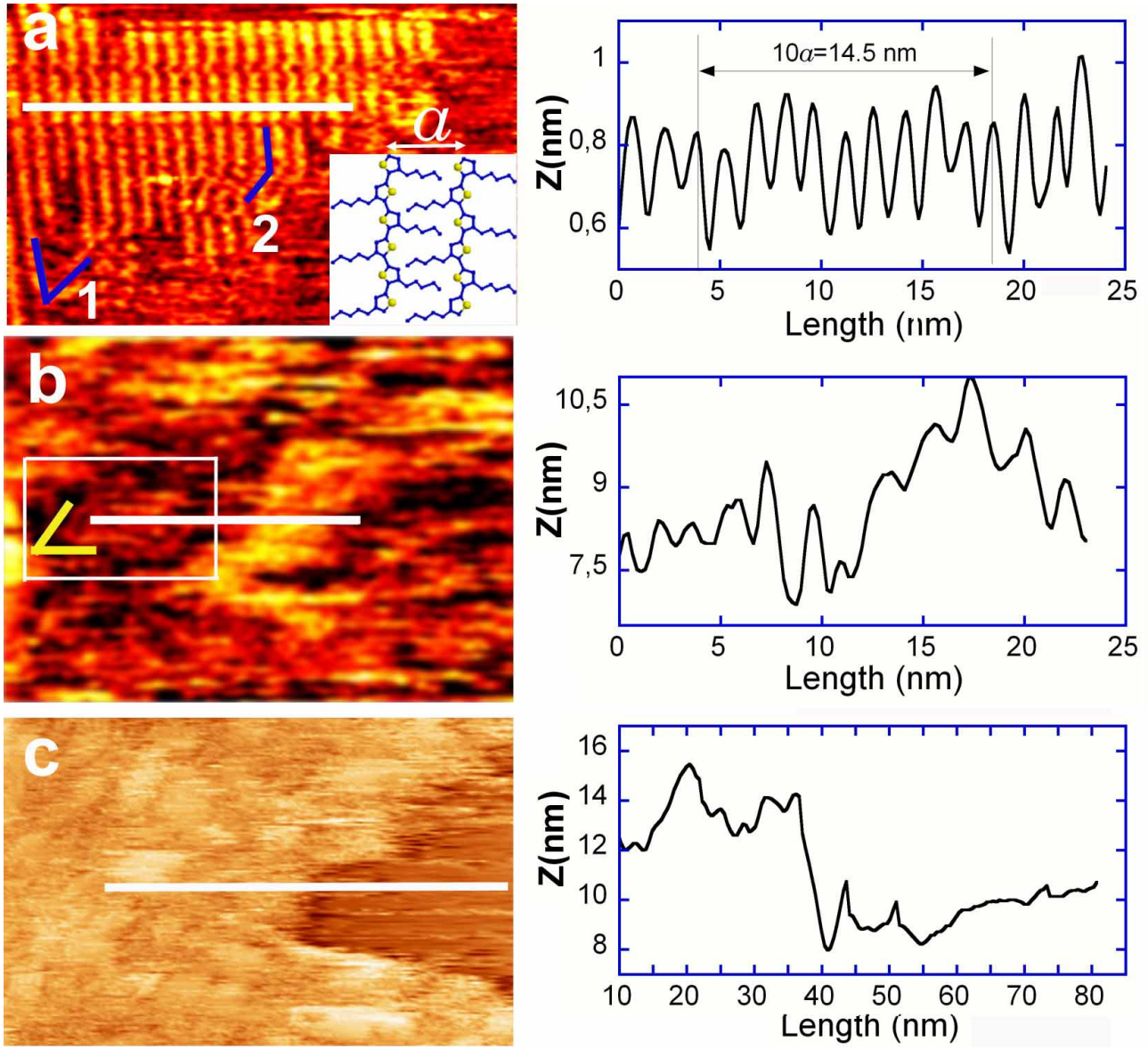
Figure captions

Fig 1 Left: series of STM images of drop cast P3HT film on HOPG. Right: line profiles along the solid white lines in each corresponding image, showing the film height variation.

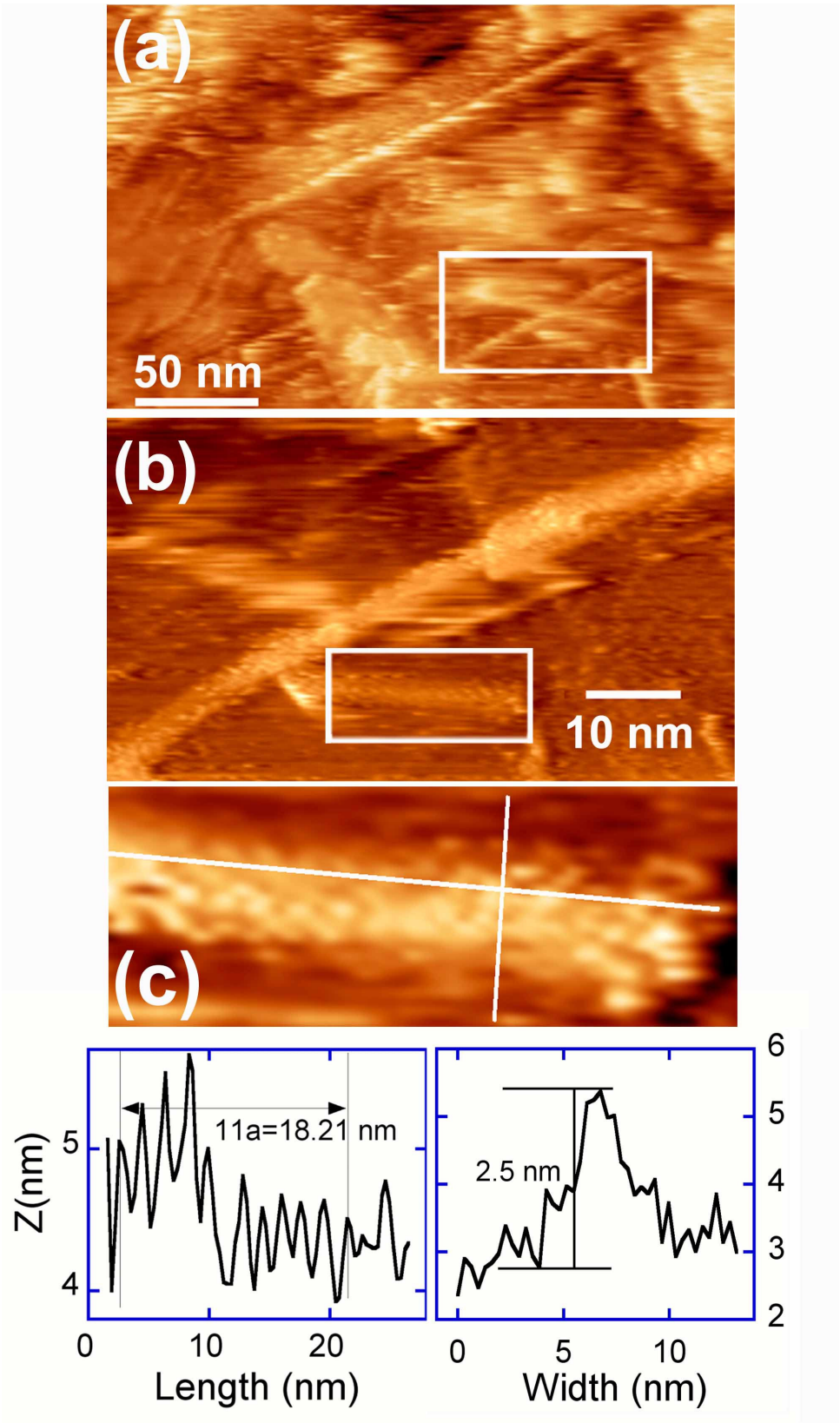
a) Monolayer P3HT film showing the interdigitated P3HT structure. 1 and 2 are 60° and 120° folding chains respectively. *Inset*: drawing of the interdigitated structure showing *a*, the chain-chain distance. From the line profile (right) *a*=1.45 nm. b) Thick polymer layer showing chains and fold of polymer chains (boxed region) appearing on the left of a thick island. V_{bias} =0.103V; *I*= 0.098nA. The line profile of the transition shows that the island sits approximately 2nm above the bottom layer. c) Thick P3HT coating showing also a bare surface region. V_{bias} =0.58V; *I*= 0.07nA. The total thickness of coating measured from the line profile is about 4 nm.

Figure 2. (a) STM image of cast film shows an abundance of nanotubes dispersed throughout the polymer matrix; V_{bias} = 0.512V; *I* = 0.053nA. (b) A close view of this nanotube reveals an ordered pattern on the tube body, along with a short tube of about 30nm; V_{bias} = 0.661V; *I*= 0.093nA . (c) Zoom of the short nanotube in (b) with cross sections: the repeat distance along the SWNT long-axis is 1.66 nm; the measured height is 2.5 nm, corresponding to the tube diameter plus the polymer thickness.

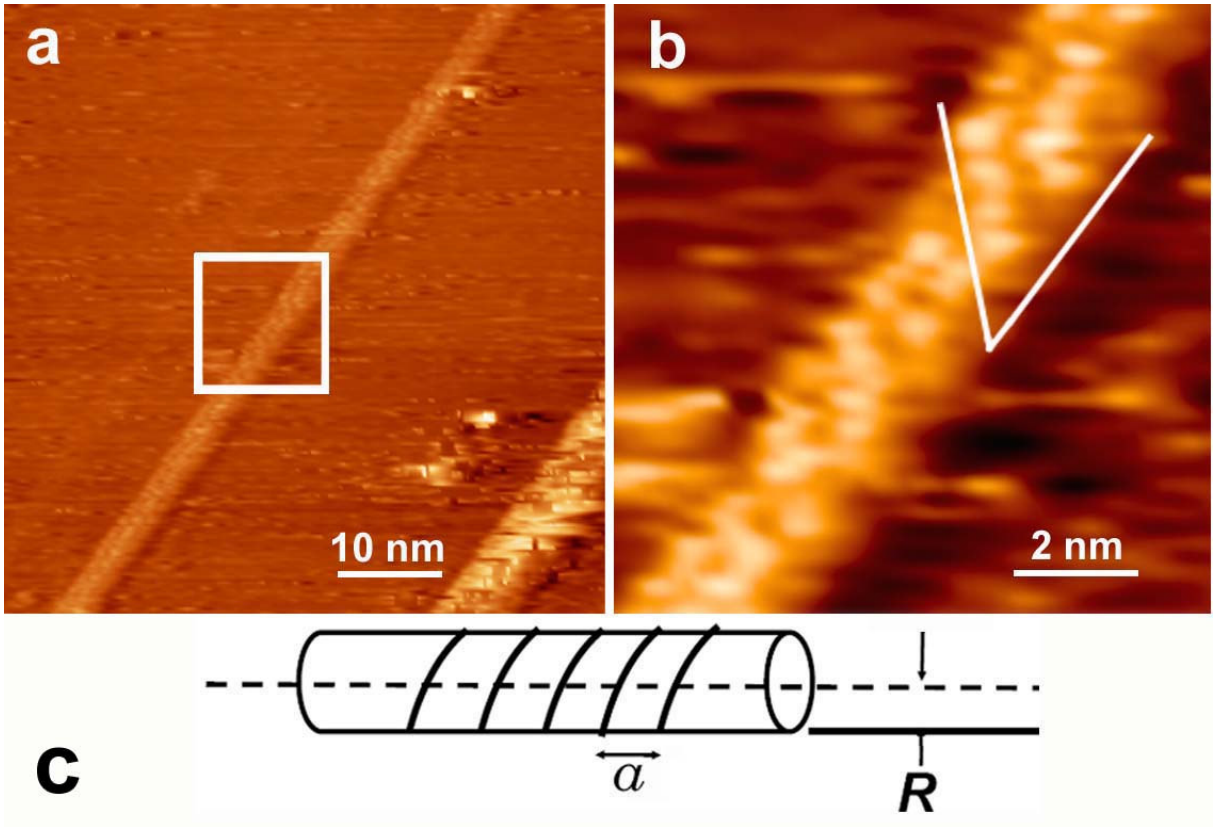
Figure 3. a) STM image of a rrP3HT-coated SWNT. (b) Zoom-in of the boxed area. The chiral angle of the polymer wrapping with respect to the nanotube long-axis is 48° as indicated in (b). STM settings: V_{bias} = 0.271V; *I*= 0.102nA. (c) sketch of P3HT wrapping around a nanotube.



R.Goh et al. Fig 1.



R.Goh et al. Fig 2



R.Goh et al. Fig 3